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OPTICAL STUDIES OF BONDING IN SOLIDS

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Optical Studies of Bonding in Solids

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The report very briefly summarizes the author's research in
The electronic structure of solid surfaces and its influence by chemisorption have become topics of rapidly growing interest. Increased attention to these questions is motivated by the desire to understand the basic processes of chemical bonding at surfaces and the need to apply this knowledge to practical use such as in catalysis. Most experimental information about electronic states near a surface comes from electron spectroscopies such as field-emission (FES) and ultraviolet photoemission (UPS), which sense primarily the density of filled electronic states near the surface. In contrast optical absorption experiments, which have proven indispensable in understanding the electronic structure of bulk solids, have seen little application to the study of surface electronic structure.

In an effort to utilize optical spectroscopy more fully in surface studies, we applied a highly sensitive reflectance technique¹ to the study of chemisorption on clean metal surfaces in ultrahigh vacuum ($p < 10^{-9}$ torr). We found²⁻⁴ that the relative reflectance changes $\Delta R/R$ due to chemisorption of small fractions ($\sim 1/20$) of a monolayer of adatoms on the surface could be detected with this technique. The observed $\Delta R/R$ was negative and as large as 1%. Furthermore, these surface effects on the reflectance can be observed on opaque substrates; hence the experiments are not limited to surface states lying within the band gap of a semiconductor or insulator. This initial work, carried out for O_2 , CO , and H_2 on $Mo(100)$, showed distinct structure in the dependence of $\Delta R/R$ on exposure e (pressure \times time). These features were attributed to the various adatom binding configurations which occur as the coverage θ increases. The changes $\Delta R/R$ saturate as the maximum coverage, a monolayer, is reached. Furthermore, the spectral dependence of $\Delta R/R$ on photon

energy $\hbar\omega$ (at full coverage) showed several structures, some of which varied with the identity of the adsorbate gas. These and other considerations led us to conclude that the observed $\Delta R/R$ in the range 2-5 eV arises from coupling to adsorbate-induced surface states within a few eV of the Fermi energy E_F .

More detailed studies have been carried out for H_2 ,⁵ O_2 , and CO adsorption on W(100).⁶ The spectral range has been extended down to 0.6 eV. Structure in $\Delta R/R(\theta)$ for H_2 adsorption indicates that the adatom binding states are more complicated than the simple two-state model previously accepted. Rather, there must exist either a third (intermediate) binding state or a continuous progression of binding states at higher θ . The spectral distribution curves $\Delta R/R(\hbar\omega)$ are dominated by strong structure which occurs below 2 eV and produces $\Delta R/R > 0$ at the lowest $\hbar\omega$ values. An oscillator analysis of the data (to deduce the surface dielectric function) suggests that this feature, common to all three adsorbates, arises from the suppression of optical transitions at low $\hbar\omega$ by the adatoms. We attribute these transitions to excitations from filled intrinsic surface states, seen in FES⁷ and UPS⁸ 0.4 eV below E_F , which are quenched by the presence of an adsorbate. Thus light couples these states primarily to final states at or just above E_F . This assignment is supported by the observation that for H_2 adsorption at low $\hbar\omega$, $\Delta R/R$ saturates at $\theta \sim 1/5$ monolayer, in the same way as the surface states in FES and UPS are quenched at this coverage. Other structures are seen at higher $\hbar\omega$ which differ somewhat with adsorbate identity and coverage. These features appear to arise from changes in the surface electronic structure which occur as the bonding of d-electrons of the surface W atoms is perturbed by the particular adsorbate to form a molecular-like complex at the surface.

These studies show clearly that high-precision reflectance measure-

ments make possible an optical reflectance spectroscopy of surfaces (ORSS) which can give valuable information about adatom binding states and the electronic structure of surfaces. As a probe of the optical excitation spectrum of the surface electronic structure, this purely optical technique yields prominent features in the joint density of surface states (optical energy gaps). Such information complements the single band density of filled surface states derived from the electron spectroscopies. We plan immediate extensions of this work which include studies of: W(110) and W(111) surfaces, where the intrinsic surface states 0.4 eV below E_F do not exist; polarization effects in $\Delta R/R$ on anisotropic surfaces; other substrates, in particular Ni and Pt; further theoretical investigation of the relation between the observed $\Delta R/R$ and local dielectric functions at the surface. The technique as now applied can be extended into the vacuum ultraviolet,⁹ and such plans are underway. Modifications of the technique will permit extension further into the infrared. Plans for the more distant future include studies of: evaporated films, cleaved, and sputter-etched surfaces of metals and semiconductors; physisorbed layers formed at low temperature; chemical reactions at surfaces involving several adsorbates.

We have also been studying the Raman and infrared spectra of amorphous Ge-Te solid solutions. GeTe is known to have different short-range order in the crystalline and amorphous forms,¹⁰ and therefore different optical properties (index of refraction, absorption edge). The light induced transition from the crystalline to amorphous form and vice-versa in Ge-Te system is therefore used in optical memories.¹¹ Our studies of lattice dynamics here contributed to the understanding of chemical bonds in the amorphous Ge-Te system. They support the random covalent network of Ge and Te atoms always 4- and 2-fold coordinated throughout the composition range.¹² The paper was accepted for presentation at the 5th International

Conference on Amorphous in Liquid Semiconductors at Garmisch-Partenkirchen and will be published in the Proceedings.¹³

We have started to apply the X-ray photoemission method to studies of chemical bonding and electronic structure of solids. One group of problems is associated with the studies of the densities of electronic states in the valence bands. This method was applied to resolve the problem about the nature of the valence bands in As_2S_3 . The vitreous modification is an important optical material whose electronic structure is not yet sufficiently understood. The preliminary results on amorphous As_2S_3 show a band corresponding to lone pair electrons in S, a band associated with the As-S bonds (as observed before¹⁴) and deeper lying well separated s-type bands of As and S observed for the first time.¹⁵

A program to investigate the trends in the valence bands and chemical shifts for the average valence V materials is under way. Results have been obtained on about 20% of the materials, including all the selenides.

The I-III-VI₂ compounds are electronic analogs of cubic II-VI compounds but they have the chalcopyrite structure. The anisotropy of this structure may be important in some applications in non-linear optical devices. The electronic structure of these materials is only partially understood.¹⁶ In particular, the influence of different composition and of different structure has not been clearly sorted out. We have been studying the reflection spectra of single crystals of CuInSe_2 -ZnSe solid solutions in the whole range of mutual solubility in a broad frequency range (0.5 to 15 eV). We can follow the changes of the optical transition energies with composition, and in particular close to the boundaries of the rather narrow immiscibility gap. At the sides of this boundary we have materials with almost the same composition but with different structures (chalcopyrite and zinc-blende, respectively). We are working on the analysis of the data with the aim to understand the changes of the electronic structure.

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2. "Optical Reflectance Studies of Chemisorption on a Clean Metal Surface," J. Anderson, G. W. Rubloff, and P. J. Stiles, Solid State Commun. 12, 825 (1973). (Reprints not yet received).
3. "Optical Spectroscopy of Surfaces: Reflectance Studies of Chemisorption," G. W. Rubloff, J. Anderson, and P. J. Stiles, Proc. of the First International Conference on Modulation Spectroscopy, Tucson, Arizona, 1972, to be published in Surface Science 37, 75 (1973). (Reprints not yet received).
4. "Vibrational Modes and Bonding in the Amorphous GeTe_{1-x} System," G. B. Fisher and J. Tauc, to be published in the Proceedings of the Fifth International Conference on Amorphous and Liquid Semiconductors, Garmisch Partenkirchen, 1973.
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6. "Analysis of Optical Reflectance Spectroscopy of Surfaces (ORSS) Data for Chemisorption," G. W. Rubloff, J. Anderson, M. A. Passler, and P. J. Stiles, to be published as an extended abstract in the Proceedings of the 20th National Vacuum Symposium of the Am. Vac. Society New York, 1973.

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